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# Thermochemical Conversion of Biomass to Ethanol

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## Summary

Thermochemical conversion of biomass to ethanol should be considered as an alternative to the conventional fermentation technologies. The thermochemical conversion of biomass consists of three steps: the hydrolysis of holocellulose to five and six carbon sugars, the conversion of sugars to lactate salts, and the pyrolysis of lactate to ethanol. Major coproducts of the process are acetic acid, butanediol, and an oxygenated hydrocarbon which has not been completely identified. A preliminary economic evaluation indicates that the overall process has economically attractive features.

## INTRODUCTION

This paper presents a novel concept for the manufacture of ethanol by thermochemical means, rather than the conventional fermentation of biomass-derived sugars. Although the research is still in the early stages, our preliminary evaluation indicates that the thermochemical process provides a promising alternative to the more conventional fermentation routes.

In recent years there has been much research on technologies to make ethanol from biomass (lignocellulose). Most of the research has concentrated on a fermentation approach, which usually consists of two steps. The first step is hydrolysis of cellulose to fermentable sugars, and the second step is the fermentation of the sugars to ethanol. Both acid and enzyme catalyzed hydrolysis of cellulose have been investigated. In some schemes, the hemicellulose is hydrolyzed to a mixture of sugars containing mostly pentose which may be fermented by some microorganisms. In general, however, the microorganisms used for fermentation of sugars to ethanol cannot ferment pentose. There has been considerable research into the fermentation of xylose and other five carbon sugars, but the processes employing new pentose fermenting microorganisms are far from commercialization.

In evaluating several processes for the manufacture of fuels and chemicals from biomass, we have observed that the raw materials are always a major cost item. Therefore, it is imperative to obtain the best utilization of raw materials possible. In the case of lignocellulosic feedstocks, this means using the

pentoses from the hemicellulose as well as using the hexoses from the cellulose.

## THERMOCHEMICAL PROCESS

### Process Concept

Whereas the conventional fermentation approach to the manufacture of ethanol uses two steps (hydrolysis and fermentation), the thermochemical concept employs three steps: hydrolysis, lactate formation, and lactate pyrolysis.

The hydrolysis of lignin cellulosic biomass may be accomplished with either acid or enzymes or with a combination of the two. The hydrolysis step would be essentially the same as that used for a fermentation process, except that higher concentrations of sugars can be tolerated in the subsequent thermochemical steps. For the purposes of our analysis we have assumed that a neutral solution of sugars containing 4% pentose and 6% hexose would be obtained from the hydrolysis of wood.

It has been known for some time that sugars will decompose to lactate when heated in the presence of base. Data in the literature indicate that the twelve carbon sugars give higher yields of lactate than the six carbon sugars. We have found that five carbon sugars can also be converted to a mixture of lactate and acetate in the presence of base. The major chemical reactions are

$$C_6H_{12}O_6 + M_2O \longrightarrow 2CH_3CH(OH)COOM + H_2O$$

$$C_5H_{10}O_5 + M_2O \longrightarrow CH_3CH(OH)COOM + CH_3COOM + H_2O$$

Some acetic acid is also made as a by-product of the conversion of glucose to lactate. The conversion of lactate to ethanol proceeds by the following reaction

$$2CH_3CH(OH)COOM + H_2O \longrightarrow 2C_2H_5OH + M_2CO_3 + CO_2$$

In addition to ethanol, the reaction mixture also contains 2,3-butanediol and an oxygenated hydrocarbon. We have not yet obtained a positive identification of the oxygenated hydrocarbon. The oxygenated hydrocarbon appears to contain both hydroxyl and carbonyl oxygen.

### Conceptual Process

A conceptual process design was based upon the experimental data. A simplified diagram of the conceptual process is shown in Figure 1. A solution of pentose and hexose sugars are received from a wood hydrolysis plant and mixed with hydrated lime. The reaction mixture is heated to 200°C and sent to a reactor where the mean residence time is 10 min. The reaction mixture is cooled, and light by-products are removed in a flash drum and sent to the boiler for use as fuel. The reaction mixture is then concentrated in an

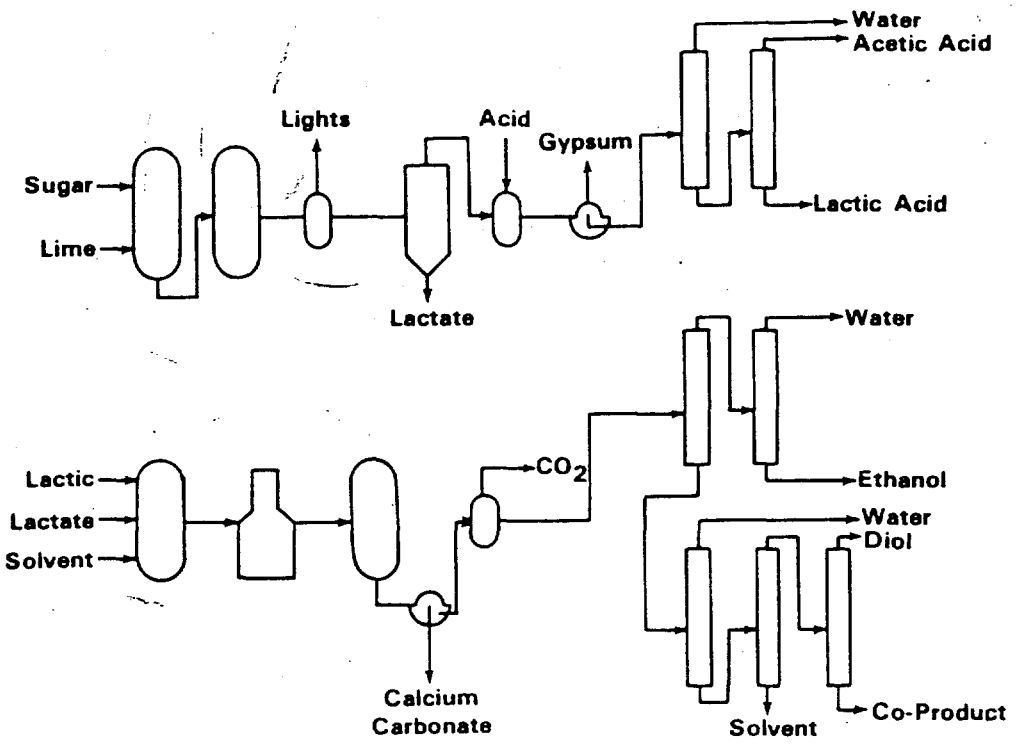


Fig. 1. Conceptual process.

evaporator-crystallizer. Calcium lactate is recovered from the crystallizers and sent to the second part of the process. The soluble lactate and acetate salts are acidified with sulfuric acid. The calcium is precipitated as gypsum and is removed by filtration. Water and acetic acid are distilled from the lactic acid. The distillation is designed to produce glacial acetic acid (minimum 99.5%) which should meet standard commercial specifications. The lactic acid is forwarded to the second stage of the process. Most of the acetic acid is derived from the pentose, since 1 mole of pentose reacts to form 1 mole of lactate and 1 mole of acetate.

The second part of the process is the conversion of lactate to alcohols. The calcium lactate and lactic acid are dissolved in a solvent. The reaction mixture is then heated to 280°C in a series of heat exchangers and a fired heater. The reaction mixture is then held at 280°C for 1 h. After the reaction, volatile materials are flashed from the reaction mixture and the solids are concentrated in hydroclones. The liquid streams are cooled and the solid calcium carbonate is removed by filtration. The liquids are then sent to a series of distillation columns where fuel grade ethanol (99.5%) is recovered. The coproducts butanediol and the oxygenated hydrocarbon which was assumed for design purposes to have the distillation characteristics of butanetriol, are also recovered. The solvent is recycled.

The portions of the plant which come in contact with acidic solutions (lactic and acetic acids) are constructed of 304 stainless steel. The remainder of the plant is carbon steel.

## PROCESS ECONOMICS

### Base Case

A preliminary economic evaluation of the process was made in order to guide the research. Since the objective of the economic evaluation was to determine the viability of the technology if the process research were successful, some optimistic assumptions were made for the base case. These optimistic assumptions related primarily to the yield obtainable and to the price of raw materials. We assumed that a 10% sugar solution would be available from a wood hydrolysis system at a cost of 4.24¢ per pound contained sugar (hexose plus pentose). Implicit in this assumed price is the successful development of an economic hydrolysis system [1]. The sensitivity to our optimistic assumption of sugar cost, and to other key assumptions, is explored in a later section.

The assumed yields of lactate from the sugars for base case economics and the best experimental results are compared in Table I. Essentially theoretical yields were obtained for the conversion of xylose to lactate, while the yields from glucose were somewhat less than expected. While the economic evaluation assumed a yield of 0.83 g lactic acid per gram glucose, the best experimental yield achieved was about 0.5 g/g. Nevertheless, this is significantly better than yields reported in the literature which are 0.15–0.31 g/g [2,3]. We anticipate that further research would increase the yield of lactic acid towards the level assumed for the economic evaluation.

The yield of products for the lactic pyrolysis assumed for the economic evaluation was based on actual experimental results. This results in an overall yield of the process of 63% as shown in Table II. It was assumed that acetic acid could be sold for its list price of $0.265 per pound and that ethanol and all other products could be sold for $0.257 per pound, which is equivalent to ethanol at $1.70 per gallon, for the base case.

The processing facility for the economic evaluations was sized to take the sugars from a wood hydrolysis plant processing 1,000 dry tons per day. These sugars can then be converted to 329 million pounds of products with the distribution shown in Table II. This is a fairly large chemical processing facility, which will make 117 million pounds of acetic acid and 58 million pounds of ethanol per year. By way of comparison, the wood hydrolysis section would be equivalent to a typical modern paper mill.

**TABLE I**

Yield of Lactate from Sugars

| Sugar | Yield, g lactic acid/100g sugar | |
|---|---|---|
| | Experimental | Base Case Economics |
| Hexose | 48 | 83 |
| Pentose | 60 | 60 |

**TABLE II**

Base Case Material Balance[a]

| | |
|---|---|
| Raw Materials | |
| Hexose | 60.6 |
| Pentose | 39.4 |
| | 100.0 |
| Products | |
| Acetic acid | 22.4 |
| Ethanol | 11.1 |
| Butanediol | 2.9 |
| Oxygenated hydrocarbon | 26.6 |
| | 63.0 |

[a] Basis: 100 lb sugar.

The capital requirements for a plant to produce 329 million pounds of products per year are presented in Table III. These capital costs are in 1982 dollars and exclude investment for wood hydrolysis. The fixed capital requirement for off-sites is about twice the capital required for the battery limits process. The largest single cost is the steam plant, which generates 335 thousand pounds steam per hour and costs $21.5 million. Since the steam plant is such a major cost item, future optimization of the heat balance could result in a significant reduction in the total capital cost. Cooling towers and storage tanks are also significant off-site costs. There is no single item which dominates the costs of the battery-limits process equipment. As would be expected from examining the flow sheet (Fig. 1), the cost of separations is quite high for this process. (The reader should, however, recall that most of the water in the original feed was removed prior to distillation). Working capital estimates

**TABLE III**

Capital Requirements (Million 1982 $)

| | |
|---|---|
| Fixed Capital | |
| Battery Limits | 18.4 |
| Offsites | 34.1 |
| Contingency @ 20% | 10.5 |
| | 63.0 |
| Working Capital | 5.8 |
| Total Capital | 68.8 |

includes a five-day inventory of sugars plus a fifteen-day inventory of other raw materials and products. Spare parts inventory was estimated at 1% of total fixed capital and net receivables were estimated to be equal to 15 days product at manufacturing costs.

The manufacturing costs for the base case are summarized in Table IV. The cost of sugars represent over 40% of the manufacturing cost, therefore the total conversion of sugars is a key factor in the overall economics. The total annual manufacturing costs, including all direct costs plus estimated sales, administration and research costs, but excluding depreciation and before tax profit, is $51.8 million.

Assuming acetic acid can be sold at $0.265 per pound and that ethanol and

**TABLE IV**

Manufacturing Costs

| | Unit Cost | $1000/yr |
|---|---|---|
| Raw Materials | | |
| Hexose | 7¢/lb | 22,176 |
| Pentose | 0 | -- |
| Lime | $32/ton | 2,807 |
| Makeup Solvent | $0.485/lb | 4,022 |
| Sulfuric Acid | $77/ton | 3,844 |
| Subtotal Materials | | $32,849 |
| Coal | $1.75/MM Btu | 5,463 |
| Natural Gas | $3.00/MM Btu | 2,351 |
| Cooling Water | $0.048/1000 gal. | 18 |
| Boiler Feedwater | $1.18/1000 gal. | 19 |
| Subtotal Materials & Fuels | | $40,700 |
| Direct Operating Labor | $15/hr | 1,901 |
| Supervision | | 285 |
| Overhead | | 729 |
| Maintenance | | 1,759 |
| Misc. Supplies | 30% operating labor | 570 |
| Insurance + Taxes | | 1,101 |
| Direct Manufacturing Cost | | $47,045 |
| Sales, Admin. & Research | 5.5% sales | 4,725 |
| | | $51,770 |

other products can be sold at $0.257 per pound, and assuming a 10% tax credit, five-year accelerated depreciation, fifteen-year economic plant life, and a 50% effective income tax rate, then the internal rate of return is 34%.

## Sensitivity of Economics

The sensitivity of the internal rate of return to several of the more important process parameters was explored. Because the research is still in an early stage, there are many unanswered technical questions, and it was expected that a sensitivity analysis would identify those technical issues which should be emphasized in future work. In addition, there are some uncertainties regarding the economics which have yet to be resolved, e.g., optimized heat recovery.

The internal rate of return appears to be relatively insensitive to the capital investment. Figure 2 indicates that even if the fixed capital investment were increased by over 50%, the internal rate of return would still exceed 30%. The circle on Figure 2 and the following figures indicates the base case internal rate of return of 34%.

As noted earlier, sugar price represents over 40% of the base case manufacturing cost. The profitability is quite sensitive to sugar costs, as illustrated in Figure 3. Nevertheless, even if the sugar price were to increase from the average of 4.24¢ per pound assumed in the base case to 8¢ per pound, the internal

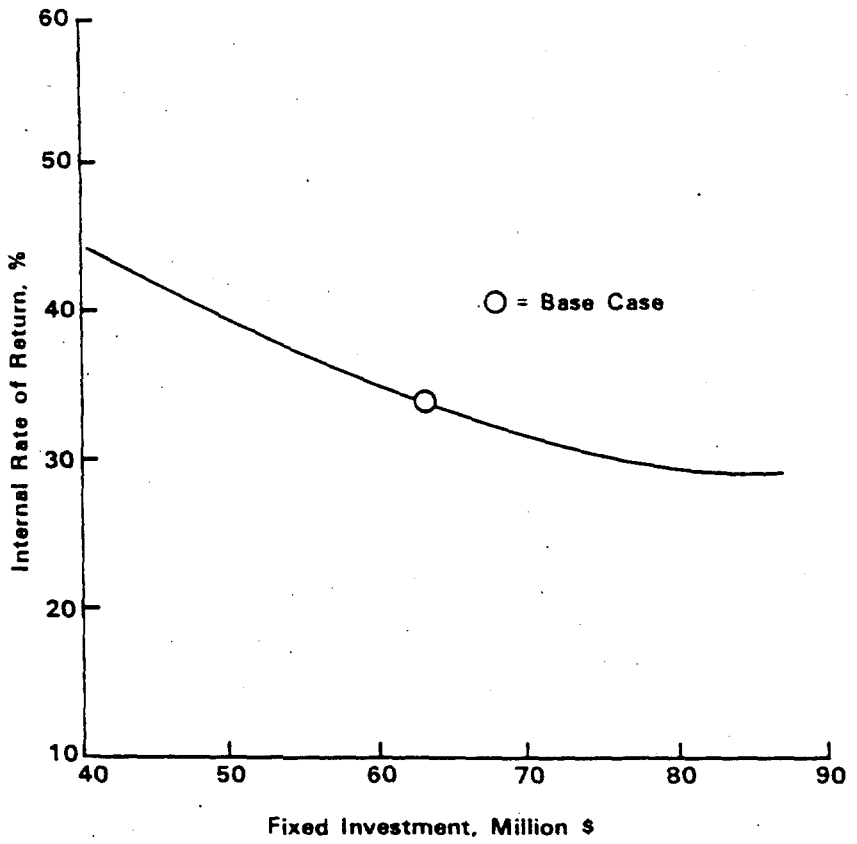


Fig. 2. Sensitivity of internal rate of return to fixed capital.

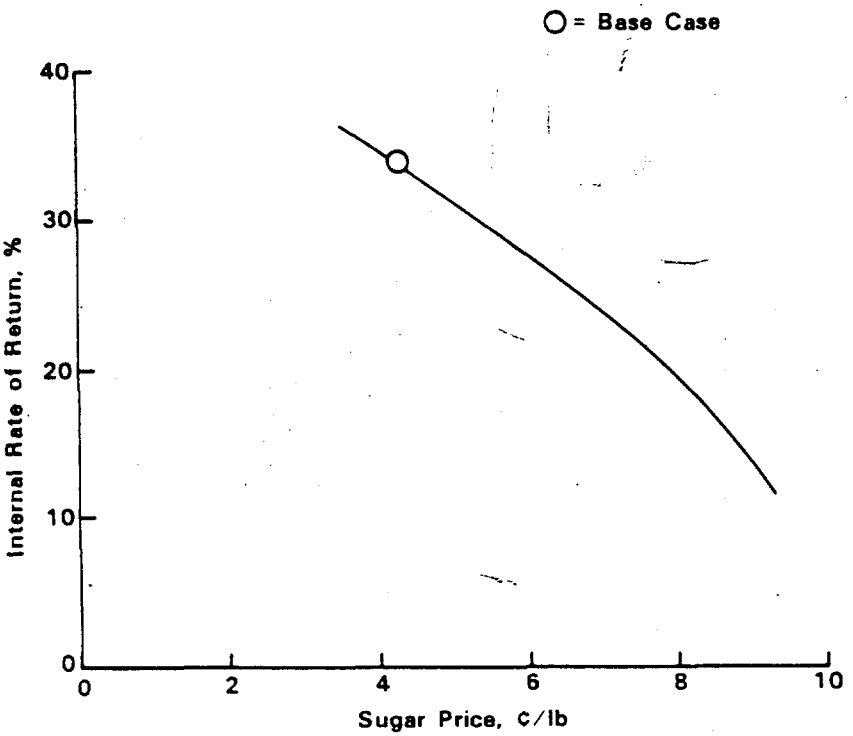


Fig. 3. Sensitivity of internal rate of return to sugar prices.

rate of return would still be about 20%. At a total sugar price above 8¢ per pound, the profitability drops rapidly. It should be remembered that this is the price of mixed sugars (hexose + pentose) in solution. The cost of dry, crystalline sugars would be considerably higher. Roberts *et al.* [1] estimated that hexose could be made in 13% solution by acid hydrolysis of wood for about 10¢/kg (4.5¢/lb). These costs were for a plug flow reactor at 20% solids. If these costs can indeed by achieved, then mixed sugars should be even less expensive. By way of comparison, the world price of raw sugar in mid 1982 was 7¢/lb [4]. This is for crystalline sugar, not a solution.

The profitability of the process is also quite sensitive to the yield of products. The product yield assumed for the base case is shown in Table II. Overall, it was assumed that 63% of the sugars were converted to useful products. This is based upon extrapolation of experimental results and upon the assessment of the scientists involved in developing the process. Actual yields obtained to date are in the range of 45 to 50% of the sugars. Yields are better with pentose than with hexose. As illustrated in Figure 4, at a yield of 50% salable products from sugars, the internal rate of return drops to about 21%. At a 45% yield, the internal rate of return is about 14%.

It seems that the assumption that butanediol and the oxygenated hydrocarbon would be at least as valuable as ethanol is reasonable. Butanediol would have a heating value similar to that of ethanol when blended with gasoline. The oxygenated hydrocarbon would be expected to make an excellent solvent. By way of comparisons, other solvents in the same general molecular weight range have list prices ranging from 36 to 80¢ per pound. It is possible that the

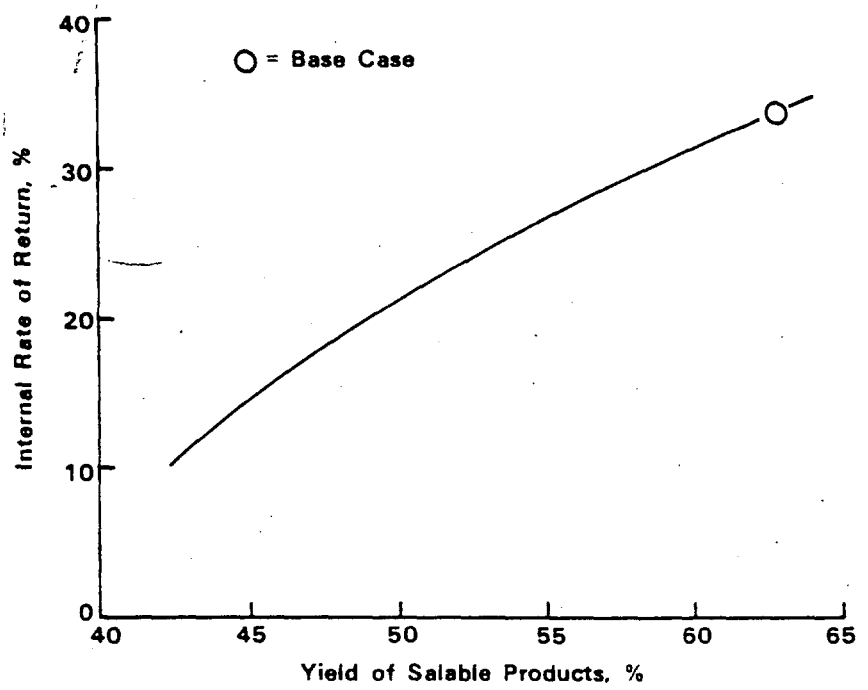


Fig. 4. Sensitivity of return to yield of salable products.

oxygenated hydrocarbon is an intermediate which could be recycled to the process. In this event, its value would be slightly less than that of ethanol.

Figure 5 shows the sensitivity of internal rate of return of pretax net income. This figure is also useful for evaluating the sensitivity to the prices of the butanediol and the oxygenated co-product. The circle in Figure 5 repre-

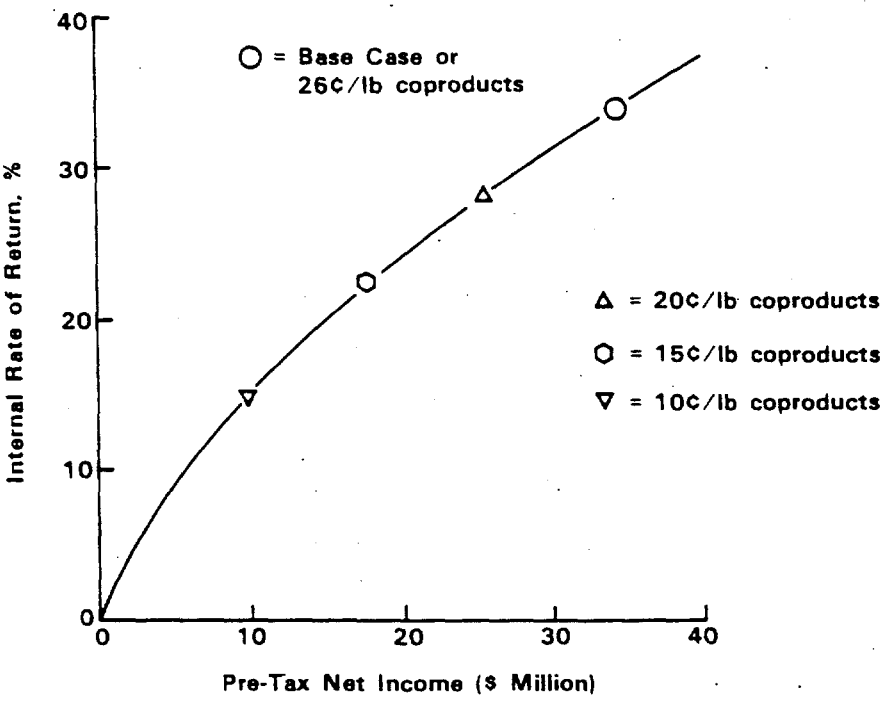


Fig. 5. Sensitivity of internal rate of return to pretax net income.

sents the base case in which butanediol and the unknown were assumed to have a value of 26¢ per pound. The triangle illustrates the rate of return if the butanediol and the unknown compound have a value of 20¢ per pound. In that case, the internal rate of return would decline to about 28%. The square represents these coproducts valued at 15¢ per pound; the inverted triangle values them at 10¢ per pound.

## CONCLUSIONS

The preliminary research and economic evaluation on the thermochemical route from biomass to ethanol have shown that this is a promising technology which offers an alternative to conventional fermentation. More work is needed to refine the technology and to optimize the process. Areas of needed research include positive identification of the oxygenated hydrocarbon coproduct and optimization of the solvent selection.

The ability to convert pentose to useful products is one of the major features of this technology.

The steps in the thermochemical conversion can be used either in conjunction with or as an alternative to fermentation technology. For example, it may be desirable to use this process for pentoses in combination with a hexose fermentation.

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